

FEDERAL REPUBLIC OF GERMANY

Certificate

On September 11, 1998 the Institut für Angewandte Chemie Berlin-Adlershof e.V. in Berlin/Germany filed a patent application entitled

"Method For Producing Active And/Or Selective
Solid Catalysts from Inorganic Or Organometallic
Solid Materials or Mixtures Thereof"

with the German Patent and Trademark Office.

The attached documents represent are a true and accurate rendition of the original documents of this patent application.

The application was given the provisional serial number B 01 J 37/00 of the International Patent Classification, by the German Patent and Trademark Office.

Munich, November 3, 1999

German Patent and Trademark Office

The President

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Method For Producing Active And/Or Selective Solid Catalysts
From Inorganic Or Organometallic Solid Materials
or Mixtures Thereof

Specification

The invention relates to a method for a fast and economic development of solid catalysts for heterogeneous catalytic reactions, occurring in processes in the chemical production and in the refinery technology as well as in environmental technology, by their parallel testing according to evolutionary methods.

The new development or improvement of heterogeneous inorganic solid catalysts is based on empirical expert knowledge and basic knowledge. Even though a comprehensive basic knowledge is available in regard to the function of individual inorganic components or compounds in the catalysis of certain partial reaction steps, which is of decisive importance for the catalyst development, it cannot be avoided in practice within the near future to prepare a large number of catalysts which are comprised of different active components or phases and to test them with regard to the catalytic action for the reaction in consideration.

For carrying out a predetermined reaction, several catalytically active phases will generally be available which are produced in a suitable manner and in a ratio of the active components to be empirically determined and which are combined in this way. The knowledge of physical, physical-chemical, and catalytic properties of solid bodies forms a rational basis for the selection of catalytically active materials in the catalyst development and improvement. Even when in an ideal situation the correct individual components or individual phases of the catalyst can be selected, it is required to determine the suitable mass ratio and preparation method.

A suitable method for such optimization problems is the application of combinatorial and evolutionary methods

(Ugi, I. et al., *Chimia* **51** (1997) 39 - 44). These algorithms have been employed in the past in biochemistry and active ingredient research in order to select within a time as short as possible new substances with a desired specific activity from a plurality of compounds. These principles have also been used in the meantime in the development of homogenous catalysts (DE-A 197319904). In the aforementioned applications the substances to be examined are always in solution. The activity range of the desired property (e.g., catalytic activity and selectivity) is limited to a molecule whose optimal element composition and structure is to be found.

In contrast to this, in the heterogeneous catalysis the object is to select the catalytically most effective inorganic solid materials and to determine their optimal weight proportion in the final catalyst. By application of evolution strategies in the development of heterogeneous catalysts, the experimental expenditure in the catalyst development is to be reduced, on the one hand, and the probability of finding an optimal catalyst is to be increased, on the other hand, in comparison to the currently still substantially empirically oriented methods employed in practice.

The combinatorial approach is an effective developmental strategy when a large number of parameters affect the properties of products. Despite the great success of this strategy in the development of new medicaments, the application of combinatorial methods in the inorganic chemistry and catalysis is a new field. The first application of combinatorial methods in the development of new solid materials was reported in the year 1995 by Schultz et al., *Science*, **268** (1995) 1738 and *Science* **270** (1995) 273. The authors have demonstrated that the solid material libraries can be tested with respect to superconductivity and magneto resistance. In the same year, libraries of complexes for the selective bonding of metal ions as well as of phosphine-containing peptide ligands for the Rh(I)-catalyzed hydrogenation of methyl-2-acetamido acrylate to N-acetyl alanine methyl ether were established.

The synthesis of libraries containing a large number (up to 26,000) of combinations of inorganic materials on a silicon

matrix has been described (E. Danielson et al., Nature **389** (1997) 944). This technology was tested, inter alia, on the example of heterogeneous catalytic CO oxidation for determining analytically active solid materials. The appropriate solutions of Pt, Pd and Rh precursor mixtures were brought up as thin layers by automatic synthesis in 144 holes (12 x 12) on a quartz substrate. The integrated substrate was reduced in H₂ strain at 800° Celsius to receive thin layers of metal catalysts, which substrate was used in the CO oxidation at 350° - 450° Celsius. Analysis was made by scanning mass spectrometer. This allowed the analysis of each library member with the help of a quartz capillary tube. The obtained results were represented in three-dimensional diagrams from which the combinations which resulted in high CO₂ yields and thus an increased catalytic activity could be determined.

Moreover, a synthesis of a library of polyoxy metallates with Keggin structure have been described (C.L. Hill et al., J. Mol. Catal. A **114** (1996) 114); 39 homogeneously dissolved catalysts were prepared by mixing aqueous solutions of Na₂MoO₄·2H₂O, NaVO₃ und Na₂MPO₄ (M = W, Mo). The resulting solutions were used without further treatments in the aerobic oxidation of tetrahydro thiophen to sulfoxide at 95°. The educt conversion and the product formation were determined by means of the GLC analysis and presented as a three-dimensional „reaction histogram„ (x-axis - Mo/W content; y axis - V content; z axis - product yield). Since with most catalysts comparable results were obtained, no sound conclusion could be drawn.

A combinatorial strategy has been used by Mallouk et al. (Fuel Cell Seminar: Orlando, Florida (1996) 686) in the development and optimization of alloys of three metals which are used as anode materials in the electrochemical oxidation of methanol. For the preparation of libraries (9 arrays with 135 compositions) five noble metals (Pt, Ru, Os, Rh, and Pd) were used. The appropriate solutions were brought up on a matrix and after that dried and reduced. The characterization of the single compositions took place by XRD, SEM and EDAX. The libraries were tested in an electrochemical cell. The pH value changes because of reaction by producing protons. By

use of a pH fluorescence indicator the active compositions could be recognized by visual analysis under UV radiation. The results have shown that Pt/Rh/Os and Pt/Ru/Os are promising. This work is an example for an effective parallel
5 testing.

Combinatorial libraries of metal catalysts supported on Al_2O_3 (inter alia Bi, Cr, Co, Cu, Ni, Pd) with 16 elements of a matrix are used by Willson et al. in the hydrogen oxidation reaction. The reactor was furnished with a special camera for
10 the in-situ IR thermography; the catalytic activity was therefore determined via the ignition temperature. A disadvantage of the analytical method employed in this work is that the information in regard to product selectivity is missing.

15 In the above described methods of a combinatorial approach and their use for determining active compounds and optimized catalysts, very many syntheses for these target materials are performed which are time-consuming and material-intensive.

20 It is therefore an object of the invention to develop a method for preparing heterogeneous solid catalysts for a predetermined reaction by use of combinatoric and evolutionary methods.

25 According to the invention the following procedure is followed:

- (i) preparing substance libraries of individual catalytic materials and their mixtures,
- (ii) testing of materials, i.e., individual materials and their mixtures of these substance libraries, with regard to
30 their catalytic activity,
- (iii) determining the chemical structure of the catalytically active materials,
- (iv) carrying out an iterative repetition of the steps (i) to (iii) or also (iv), based on the results obtained according to
35 (ii) and (iii), with the goal of catalyst optimization.

This procedure can be realized or practically applied in the development of heterogeneous catalysts as follows:

In the first step (i) primary components (individual materials or catalytically active phases), which have already

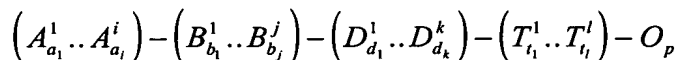
been described or are known or have been determined empirically or intuitively for the individual reactions steps of the heterogeneous catalytic reaction under consideration, are selected and introduced into the substance library; wherein by a random selection arbitrary mixtures of these individual materials are produced. In the second step (ii) these materials finally determined and prepared in this way (first generation of catalysts) are catalytically tested; these two procedures, i.e., preparation and testing, are performed parallel as much as possible, respectively. The successful materials with respect to catalysts optimization of the step (ii) are physically and physical-chemically characterized in particular with respect to their reproducible preparation in step (iii) and present the foundation for the subsequent second generation of catalysts. This second generation is generated according to methods of biological evolution from the successful materials of the first generation and then subjected to the steps (ii) and (iii).

In the second and the subsequent iterations, the most successful catalysts of all generations are employed as a foundation, respectively, whose total number relative to the total number of catalysts of a generation, however, is generally small. In general, it will be 10 to 20 % of the catalysts of one generation.

The described iterations are performed until no improvement of the catalytic behavior of the materials with respect to activity and/or selectivity for the reaction under consideration can be determined anymore.

The method for selecting components for the preparation of active and/or selective solid catalysts of inorganic or organometallic materials or mixtures thereof is comprised advantageously of the following

(a) for a catalytic reaction a number n_1 of solid catalysts of the elements of the periodic table of the elements (PTE) in the form of compounds



are prepared, wherein $A^1 \dots A^i$ are i different main components which are selected from groups of the elements of

Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number i is between 1 and 10,

5 $B^1 \dots B^j$ are j different minor components selected from the group of the elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te,

10 F, Cl, Ce and Nd and the number j is between 1 and 10,

$D^1 \dots D^k$ are k different doping elements which are selected from the group of the elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd,

15 Hg, B, Al, Ga, In, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number k is between 1 and 10,

$T^1 \dots T^l$ are l different support components which are comprised of oxides, carbonates, carbides, nitrides, borides of the elements Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or a mixed phase of two or more thereof, and the number l is between 1 and 10,

and O is oxygen,

$a_1 \dots a_i$ are identical or different mole fractions of 0 to 100 mole-% with the provision that the mole fractions $a_1 \dots a_i$ cannot all at the same time be 0,

$b_1 \dots b_j$ are mole fractions of 0 to 50 mole-%,

$d_1 \dots d_k$ are mole fractions of 0 to 10 mole-%,

$t_1 \dots t_l$ are mole fractions of 0 bis 99.99 mole-%,

p is a mole fraction of 0 to 75 mole-%, wherein the sum of all mole fractions $a_i + b_j + d_k + t_l$ may be not greater than 100 %, and

the number n_1 of catalysts with different weight composition and/or different chemical composition is in the range of 5 to 100,000, preferably in the range of 5 to 100;

35 (b) the activity and/or selectivity of the n_1 solid catalysts prepared according to (a) of the first generation is determined experimentally for a catalytic reaction in a reactor or in several reactors switched parallel;

(c) a number of 5 - 30 % is selected as number n_2 from the number n_1 of the catalysts of the first generation having the highest activities for a specific reaction and/or highest selectivities for the desired product or product mixture of the catalytic reaction;

(d) the catalyst components contained in the number n_2 of the catalysts with a pre-set probability W , which results for each of the components $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k$ and $T^1 \dots T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_2} \cdot 100\%, W_B = \frac{1}{j \cdot n_2} \cdot 100\%, W_D = \frac{1}{k \cdot n_2} \cdot 100\%, W_T = \frac{1}{l \cdot n_2} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_2 with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ and/or that the amount

of mass $a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ of the catalyst components $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k$ and $T^1 \dots T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ are varied in that new values for the mole

fractions $a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k, T^1 \dots T^l, a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ and p defined under (a) are produced in a number y_2 which form the catalysts of the second generation;

(e) the activities and/or selectivities of the y_2 solid catalysts of the second generation are determined experimentally for the same specific reaction as in (b) in one or more reactors;

(f) a number of the n_3 catalysts of the second generation, having the highest activities for a specific reaction and/or highest selectivities for the desired product and product mixture of all solid catalysts of the first and second generation, is selected, wherein the number n_3 is about 5 to 30 % of the number n_1 ;

(g) the catalyst components contained in the number n_3 of the catalysts with a pre-set probability W , which results

for each of the components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_3} \cdot 100\%, W_B = \frac{1}{j \cdot n_3} \cdot 100\%, W_D = \frac{1}{k \cdot n_3} \cdot 100\%, W_T = \frac{1}{l \cdot n_3} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_3 with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ and/or that the amount

of mass $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ of the catalyst components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ are varied in that new values for the mole

fractions $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula

$(A_{a_1}^1 \dots A_{a_i}^i) - (B_{b_1}^1 \dots B_{b_j}^j) - (D_{d_1}^1 \dots D_{d_k}^k) - (T_{t_1}^1 \dots T_{t_l}^l) - O_p$ with the meaning of $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$, $T^1 \dots T^l$, $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ and p defined under 1(a) are produced in a number y_3 which form the catalysts of the third generation;

(h) the activity and/or selectivity is of the y_3 new solid catalysts of the third generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(i) a number of n_{n+1} solid catalysts of the n -th generation, having the highest activities for a catalytic conversion and/or the highest selectivities for the desired product and product mixture of all solid catalysts of the first to n -th generation, is selected, wherein the number n_{n+1} is about 5 to 30 % of the number n_1 ;

(j) the catalyst components contained in the number n_{n+1} of the catalysts with a pre-set probability W , which results for each of the components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_{n+1}} \cdot 100\%, W_B = \frac{1}{j \cdot n_{n+1}} \cdot 100\%, W_D = \frac{1}{k \cdot n_{n+1}} \cdot 100\%, W_T = \frac{1}{l \cdot n_{n+1}} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_{n+1} with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$ and/or that the amount of mass $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ of the

catalyst components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$ are varied in that new values for the mole

fractions $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula

$$\left(A_{a_i}^1 \dots A_{a_i}^i\right) - \left(B_{b_j}^1 \dots B_{b_j}^j\right) - \left(D_{d_k}^1 \dots D_{d_k}^k\right) - \left(T_{t_l}^1 \dots T_{t_l}^l\right) - O_p \quad \text{with the meaning of}$$

$A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$, $T^1 \dots T^l$, $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ and p defined under 1(a) are produced in a number y_{n+1} which form the catalysts of the (n+1)-th generation;

(k) the activity and/or selectivity is of the y_{n+1} solid catalysts of the (n+1)-th generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(l) the selection according to the steps (c) + (f) + (i), the preparation of a new catalyst generation according to the steps (d), (g), (j), and the activity/selectivity determination according to the steps (e) + (h) + (k) is continued up to obtaining a catalyst generation in which the activity and/or selectivity relative to the previous generations as an arithmetic mean is not increased or no longer significantly increased (>1 %).

Advantageously, the preparation of the catalyst mixtures is carried out by mixing salt solutions of the elements of the component $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ and a subsequent thermal treatment in the presence of a reactive or inert gas phase (in the following referred to as tempering) or by common precipitation of sparingly soluble compounds and subsequent tempering or by loading the support components $T^1 \dots T^l$ with salt solutions or gaseous compounds of the components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and subsequent tempering, wherein the employed salts may be nitrates, sulfates, phosphates, carbonates, halogenides, oxalates, carboxylates or mixtures thereof or carbonyl compounds or acetyl acetates.

Further preferred embodiments are described in the subclaims.

The invention will be explained with the aid of the attached drawing. It is shown in:

5 Fig. 1 a diagram showing the change of yield of the respectively best five catalysts during the first three generations of catalyst optimization according to example 1;

The invention will be explained with the following specific example, that means the search for an optimized catalyst for the partial oxidation of propane to its oxygen derivatives which encompasses the sum of acrolein, acetic acid, and acrylic acid.

Example 1

15 The selection and mixture of individual catalyst components which are divided into main, minor, doping, and support components as well as the testing and further improvement of the catalyst mixtures with application of evolutionary optimization strategies is demonstrated.

20 First 30 catalysts (phase I), subsequently 10 catalysts (phase II), and then further 10 catalysts (phase III), comprised of main components, minor components, doping components, and support material are prepared with the goal of convert propane to its oxygen derivatives by oxidation with oxygen and to minimize the resulting oxides CO and CO₂ (compare step (a) above). The course of the process comprises the following steps and leads to the respective denoted results.

Phase I

30 **Step 1.** The main components are selected from the oxides of the elements V, Mo, Nb, Bi, P. The proportion of the main components are varied between 0 and 50 mole-%. The minor components are selected from the oxides of the elements Mn, Sb, Sn, and B. The proportions of the minor components are varied between 0 and 50 mole-%. The doping components are selected from the oxides of the elements Cs and either Fe or Co, either Ag or Cu, and either Ga or In. The proportions of the doping components are varied between 0 and 5 mole-%. As a further doping component Pd was used which was either not

introduced or introduced in an amount of 10^{-4} mole-%. As a support component Al_2O_3 was provided which was either not present or present in an amount of 50 % by weight in the catalyst.

5 The sum of all weight or mole ratios of the main, minor, and doping and support components yields always 100 %.

Step 2. The catalysts which were used for testing, were obtained according to the following manufacturing process. Compounds (oxides, oxalates, or nitrates) of the elements
10 mentioned in step 1 were dissolved in a little water or suspended, mixed with one another, and the mixture was evaporated. The resulting solid material was dried for 1 hr. at 200 °C and 3 hrs. at 400 °C, subsequently ground intensively for 1 hr. in a ball mill and tempered for 3 hrs.
15 at 600 °C in air.

Step 3. The catalysts compositions of the first generation obtained by the random-checked generators G05DZF, G05CAF, G05DYF und G05CCF of the NAG-Bibliothek (NAG FORTRAN Workstation Library, NAG Group Ltd., 1986) are compiled in
20 Table 1.

Step 4. The testing of the catalysts is carried out parallel in six quartz reactors (inner diameter 6 mm) which are introduced into the heatable and coolable fluidized sand bed for temperature control. Alternative configurations of the
25 parallel testing of the solid catalysts are possible according to the above description.

The following standard conditions were selected for the testing of the catalysts: $T = 500\text{ °C}$, $m_{\text{catalyst}} = 1,0\text{ g}$, $\dot{V}_{\text{total per reactor}} = 28\text{ ml}_{\text{STP}}\text{ min}^{-1}$ mit $\dot{V}_{\text{C}_3\text{H}_8} = 0,8\text{ ml}_{\text{STP}}\text{ min}^{-1}$, $\dot{V}_{\text{O}_2} = 5,6\text{ ml}_{\text{STP}}\text{ min}^{-1}$, $\dot{V}_{\text{H}_2\text{O}} = 12,0\text{ ml}_{\text{STP}}\text{ min}^{-1}$, $\dot{V}_{\text{Ar}} = 21,6\text{ ml}_{\text{STP}}\text{ min}^{-1}$. The catalysts were used for the reaction and tested with respect to the sum of the yields of acrolein and acrylic acid obtained under the standard experimental conditions (compare step (b) above; corresponds also to this
35 step in claim 2). The concentration of propane, propene, ethylene, the resulting oxygen derivatives as well as of CO and CO_2 was analyzed by means of a gas chromatograph and mass spectrometer.

Step 5. The results of the test of the first generation of catalysts are compiled in the form of the sum of the yield of acrolein and acrylic acid in Table 1. Significant differences in the yields of the 30 tested catalysts result. The best five catalysts (Nos. 4, 13, 17, 19, 21) all contain, with the exception of No. 13, the support component. Moreover, among these best catalysts, Mo as a main components as well as Sn as an minor component are present frequently. With the exception of Fe as a doping component, however, all employed catalyst components are still represented in the best five catalysts of the first generation.

Phase II

Step 6. The second generation of catalysts was obtained in that first the five catalysts Nos. 4, 19, 21, 13, and 17 with the highest oxygenate yield of the 30 that were previously tested were selected (compare step (c) in claim 1).

Step 7. The compositions of 10 new catalysts of the second generation were obtained in that

a) of the main, minor, doping, and support components of the five best catalysts (Table 1: Nos. 4, 19, 21, 13 and 17) six new combinations of main, minor, doping, and support components are formed (compare step (d) of claim 1), in that, for example, for the composition of the catalyst No. 1 of the second generation (Table 2) first the catalyst No. 17 (Table 1) was mixed with the main component P of catalyst No. 21 (Table 1), the minor component Sn of catalyst No. 4 (Table 1) and B of catalyst No. 21 (Table 1), the trace components Fe of catalyst No. 14 (Table 1), Co of K.19 (Table 1) and Cs and Pd of catalyst No.17 (Table 1), respectively, according to claims 2 and 3. According to these principles are determined 6 new catalyst compositions which are summarized in Table 2 (Nos. 1, 2, 3, 6, 7, 8).

b) The molar components of the main, minor, and doping components of the two best catalyst with the highest oxygenate yield (Table 1, Nos. 4 and 19) according to step (d) of claim 1 are changed. The result are the four new compositions Nos. 4, 5, 9. 10.

Step 8. With the process described in step 7, 10 new catalyst compositions were determined, prepared according to the

procedure (compare step 1), and then tested parallel under standard conditions as described in step 4 (compare step (e) of claim 1). The results are compiled in Table 2. These new catalysts contain frequently Mo as a main component and Sn as a minor component. Also, P as a main component and Co as a doping component, which already occurred with greater frequency in the best catalysts of the first generation, are also frequently contained in the new catalysts of the second generation.

Phase III

Step 9. From the quantity of the first and second catalyst generation the five catalysts were selected again which had the highest yield of oxygen derivatives (compare step (f)) of claim 1). These are the catalysts of Table 1: Nos. 4, 19, 21 and of Table 2: Nos. 2, 3. With the 10 new catalysts of the second generation initially no higher yields than with the best catalysts of the first generation are obtained. However, the catalysts Nos. 2 and 3 of the second generation displace the catalysts Nos. 19 and 21 from the third and fourth rank. See also Fig. 1.

Step 10. The composition of the 10 new catalysts to be produced of the third generation was obtained in that with the five catalysts selected in step 9 the same procedure as in step 7 was performed (see Table 3, compare step (g) of claim 1).

Step 11. The 10 new catalysts of the third catalyst generation were prepared according to procedure (compare step 1) and tested parallel under standard conditions as in step 4 (compare step (h) of claim 1). Among these 10 new catalysts there are now two (Nos. 4 and 9) with which the previously highest yields are surpassed. Accordingly, the catalysts Nos. 4 and 19 (Table 1) are displaced from the first and second rank (compare Fig. 1).

Step 12. The selection of catalyst compositions of the following generations (the n-th generation) was carried out in analogy to the steps 6 - 8, respectively, 9 - 11 in that, respectively, the five best catalysts of all already tested catalyst generations were selected and used for the determination of the composition of the 10 new catalysts of

the n-th catalyst generation (compare steps (i), (j), (k) of claim 1).

Result:

When the compositions of the five best catalysts of the first through third catalyst generation are compared, it is apparent that all catalysts contain Mo, Sn, Co, and the support component. The qualitative compositions of the three best catalysts are near identical. These catalysts contain all Mo, Nb, Sb, Sn, Co, Ga and the support component. The two best catalysts contain, in addition, also the doping components Cu and Pd. This underscores that the catalyst compositions with increasing generation number approximate one another, i.e., disruptive components are no longer considered during the course of optimization and the components of the catalysts with high oxygenate yield are more strongly taken into consideration upon determination of new catalysts compositions. On the basis of this evolutionary strategy, already in the third catalyst generation a 100 % higher oxygenate yield than in the first generation is obtained (Fig. 1).

First Catalyst Generation

Yield of C₃ Rank among
oxygenates the five best
Catalyst

[illegible]

16	10,37	1,67	0	14,20	5,50	0	0	18,04	0	0	0,2	0	0	0	0	0	50	0	0,045	
											22									
17	8,56	2,90	0	11,06	5,40	0	0	13,55	7,89	0	0	0,1	0	0,4	0,1	0	50	0,0001	0,077	5.
												98		35	66					
18	14,11	0	5,89	17,74	0	0	9,51	1,28	0	0,3	0	0,4	0,6	0	0	0,34	50	0	0,011	
											18	95	40		0					
19	0	9,11	0	23,40	13,48	0	0	3,56	0	0	0,4	0	0	0	0	0	50	0,0001	0,215	2. 2. 4.
											66									
20	27,10	15,00	0	2,90	20,33	0	0	8,23	25,66	0	0	0,3	0	0,4	0,7	0	0	0,0001	0,015	
												18		52	00					
21	0	0	0,187	0	18,58	5,69	0	0	24,25	0	1,0	0,3	0	0	0	0	50	0	0,085	3. 5.
											69	93								
22	0	0	29,61	12,82	0	37,00	20,21	0	0	0	0,3	0	0,9	0	0	0	0	0	0,001	
											63		39							
23	0	0	0	39,59	0	3,10	55,66	0	0	0	0	1,6	0	0	0,3	0	0	0,0001	0,001	
												52		46						
24	20,70	5,98	0	27,18	12,47	33,67	0	0	0	0	0	0	0	0	0	0	0	0	0,005	
25	0	0	0	31,94	7,13	0	42,87	18,06	0	1,7	0	0	0	0	0,4	0	0	0,0001	0,018	
											23		74							
26	11,51	0	38,74	19,84	0	0	0	0,94	28,17	0	0	0,8	0	0	0	0	0	0,0001	0,002	
												01								
27	6,69	17,04	0	9,85	2,67	0	0	13,02	0	0	0,5	0	0	0	0	0,20	50	0,0001	0,014	
											31						8			

- 18 -

28	22,58	9,24	0	0	28,46	15,12	0	1,77	21,00	0	0,6	0,3	0	0,4	0,6	0	0	0,0001	0,000
											59	28		54	91				
29	0	0	19,95	0	11,41	0	2,87	15,17	0	0	0	0,5	0	0	0,2	0	50	0	0,004
												97			40				
30	29,36	11,64	0	37,17	19,45	0	0	1,73	0	0	0,6	0	0	0	1,0	0	0	0	0,002
											49						01		

Second Catalyst Generation

Yield of C₃ Rank among
oxygenates the five
best

[illegible]

- 20 -

5	0	11,79	0	11,48	1,35	0	0	24,43	0	0	0,9	0	0	0	0	50	0,0001	0,024	
52																			
6	0	4,37	3,24	7,22	12,13	0	12,80	9,93	0	0	0,3	0	0	0	0	50	0,0001	0,020	
00																			
7	0	0	0	0	26,54	0	21,71	0	0	1,2	0	0	0	4,8	0	50	0,0001	0,024	
70																			
8	6,42	6,82	0	0	13,92	4,27	0	11,39	5,91	0	0,6	0,1	0	0,3	0,1	0	50	0,0001	0,000
70																			
9	0	4,04	9,23	0	0	0	20,15	13,75	0	0	2,0	0	0	0	0,7	0	50	0,0001	0,003
90																			
10	0	3,09	0	26,10	5,85	0	0	13,69	0	0	1,2	0	0	0	0	50	0,0001	0,000	
70																			

Table 3 Third Catalyst Generation

No. Composition mole-%
(Y₃)

Yield of C₃ Rank among
oxygenates the five
best
Catalyst
Generations

Main component Minor component Doping components Su Pd mole-%

pp we
or ig
t, ht
we %
ig
ht
%

V Mo Nb Bi P Mn Sb Sn B Fe Co Cs Ag Cu Ga In

1	0	0	31,78	0	17,10	0	0	0	0	0,8	0	0	0	0,3	0	50	0,0001	0,006
										2				1				
2	0	6,34	24,05	0	12,94	0	0	5,50	0	0,6	0,1	0	0,3	0,1	0	50	0,0001	0,096
										2	4		0	2				
3	0	6,40	14,62	9,90	0	0	0	18,22	0	0,3	0,2	0	0,1	0,0	0	50	0	0,010
										8	3		2	7				
4	0	34,61	0,87	0	0	0	5,37	8,28	0	0	0,4	0	0	0,0	0,4	0	0,0001	0,821
										3			7	5				2.

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CLAIMS

1. A method for preparing active or selective solid
5 catalysts of inorganic or organometallic materials or mixtures thereof which comprises that

(a) for a catalytic reaction a number n_1 of solid catalysts of the elements of the periodic table of the
10 elements (PTE) in the form of compounds

$$(A_{a_1}^1 \dots A_{a_i}^i) - (B_{b_1}^1 \dots B_{b_j}^j) - (D_{d_1}^1 \dots D_{d_k}^k) - (T_{t_1}^1 \dots T_{t_l}^l) - O_p$$

are prepared, wherein $A^1 \dots A^i$ is a quantity i of different main components which are selected from the groups of elements, and the number i is between 1 and
15 10,

Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number i is between 1
20 and 10,

$B^1 \dots B^j$ are j different minor components selected from the group of the elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, C, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number j is
25 between 1 and 10,

$D^1 \dots D^k$ are k different doping elements which are selected from the group of the elements

Li, Na, Ka, Mg, Ca, Sr, Ba, Y, La, Ti, Zr, V, Nb, Cr, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Cd, Hg, B, Al, Ga, In, Si, Sn, Pb, N, P, As, Sb, Bi, S, Se, Te, F, Cl, Ce and Nd and the number k is
30 between 1 and 10,

$T^1 \dots T^l$ are l different support components which are comprised of oxides, carbonates, carbides, nitrides, borides of the elements Mg, Ca, Sr, Ba, La, Zr, Ce, Al, Si or a mixed phase of two or more thereof, and the number l is between 1 and 10,
35

and O is oxygen,

$a_1 \dots a_i$ are identical or different mole fractions of 0 to 100 mole-% with the provision that the mole fractions $a_1 \dots a_i$ cannot all at the same time be 0,

$b_1 \dots b_j$ are mole fractions of 0 to 50 mole-%,

$d_1 \dots d_k$ are mole fractions of 0 to 10 mole-%,

$t_1 \dots t_l$ are mole fractions of 0 bis 99.99 mole-%,

p is a mole fraction of 0 to 75 mole-%, wherein the sum of all mole fractions $a_i + b_j + d_k + t_l$ may be not greater than 100 %, and

the number n_1 of catalysts with different weight composition and/or different chemical composition is in the range of 5 to 100,000, preferably in the range of 5 to 100;

(b) the activity and/or selectivity of the n_1 solid catalysts prepared according to (a) of the first generation is determined experimentally for a catalytic reaction in a reactor or in several reactors switched parallel;

(c) a number of 5 - 30 % is selected as number n_2 from the number n_1 of the catalysts of the first generation having the highest activities for a specific reaction and/or highest selectivities for the desired product or product mixture of the catalytic reaction;

(d) the catalyst components contained in the number n_2 of the catalysts with a pre-set probability W, which results for each of the components $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k$ and $T^1 \dots T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_2} \cdot 100\%, W_B = \frac{1}{j \cdot n_2} \cdot 100\%, W_D = \frac{1}{k \cdot n_2} \cdot 100\%, W_T = \frac{1}{l \cdot n_2} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_2 with a probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ and/or that

the amount of mass $a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ of the catalyst components $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k$ and $T^1 \dots T^l$ for some of the catalysts selected with a

probability of $W_{cat} = \frac{1}{n_2} \cdot 100\%$ are varied in that new

values for the mole fractions $a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$

and $t_1 \dots t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$, $T^1 \dots T^l$, $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ and p defined under (a) are produced in a number y_2 which form the catalysts of the second generation;

(e) the activities and/or selectivities of the y_2 solid catalysts of the second generation are determined experimentally for the same specific reaction as in (b) in one or more reactors;

(f) a number of the n_3 catalysts of the second generation, having the highest activities for a specific reaction and/or highest selectivities for the desired product and product mixture of all solid catalysts of the first and second generation, is selected, wherein the number n_3 is about 5 to 30 % of the number n_1 ;

(g) the catalyst components contained in the number n_3 of the catalysts with a pre-set probability W , which results for each of the components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_3} \cdot 100\%, W_B = \frac{1}{j \cdot n_3} \cdot 100\%, W_D = \frac{1}{k \cdot n_3} \cdot 100\%, W_T = \frac{1}{l \cdot n_3} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_3 with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ and/or that

the amount of mass $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ of the catalyst components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_3} \cdot 100\%$ are varied in that new

values for the mole fractions $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$, $T^1 \dots T^l$, $a_1 \dots a_i$, $b_1 \dots b_j$, $d_1 \dots d_k$ and $t_1 \dots t_l$ and p defined under (a) are produced in a number y_3 which form the catalysts of the third generation;

(h) the activity and/or selectivity is of the y_3 new solid catalysts of the third generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(i) a number of n_{n+1} solid catalysts of the n -th generation, having the highest activities for a catalytic conversion and/or the highest selectivities for the desired product and product mixture of all solid catalysts of the first to n -th generation, is selected, wherein the number n_{n+1} is about 5 to 30 % of the number n_1 ;

(j) the catalyst components contained in the number n_{n+1} of the catalysts with a pre-set probability W , which results for each of the components $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k$ and $T^1 \dots T^l$ from the corresponding equations

$$W_A = \frac{1}{i \cdot n_{n+1}} \cdot 100\%, W_B = \frac{1}{j \cdot n_{n+1}} \cdot 100\%, W_D = \frac{1}{k \cdot n_{n+1}} \cdot 100\%, W_T = \frac{1}{l \cdot n_{n+1}} \cdot 100\%$$

are exchanged between two catalysts selected from the number n_{n+1} with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$ and/or

that the amount of mass $a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ of the catalyst components $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k$ and $T^1 \dots T^l$ for some of the catalysts selected with a probability of $W_{cat} = \frac{1}{n_{n+1}} \cdot 100\%$ are varied in that new

values for the mole fractions $a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ are determined within the limits defined under (a);

in this way new catalysts of the general formula (I) with the meaning of $A^1 \dots A^i, B^1 \dots B^j, D^1 \dots D^k, T^1 \dots T^l, a_1 \dots a_i, b_1 \dots b_j, d_1 \dots d_k$ and $t_1 \dots t_l$ and p defined under (a) are produced in a number y_{n+1} which form the catalysts of the $(n+1)$ -th generation;

(k) the activity and/or selectivity is of the y_{n+1} solid catalysts of the $(n+1)$ -th generation prepared according to (g) is determined experimentally for the same specific reaction as in (b) in one or more reactors;

(l) the selection according to the steps (c) + (f) + (i), the preparation of a new catalyst generation according to the steps (d), (g), (j), and the activity/selectivity determination according to the steps (e) + (h) + (k) is continued up to obtaining a catalyst generation in which the activity and/or selectivity relative to the previous generations as an arithmetic mean is not increased or no longer significantly increased.

2. The method according to claim 1, wherein the preparation of the catalyst mixtures is carried out by mixing salt solutions of the elements of the components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and $T^1 \dots T^l$ and subsequent thermal treatment in the presence of a reactive or inert gas phase (tempering) or by common precipitation of sparingly soluble compounds and subsequent tempering or by loading of the support component $T^1 \dots T^l$ with salt solutions or gaseous compounds of the components $A^1 \dots A^i$, $B^1 \dots B^j$, $D^1 \dots D^k$ and subsequent tempering, wherein the employed salts are nitrates, sulfates, phosphates, carbonates, halogenides, oxalates, carboxylates, or mixtures thereof or carbonyl compounds or as acetyl acetonates.

3. The method according to claim 1 or 2, wherein the preparation of new catalyst mixtures of the 2nd to the n-th generation takes place by mechanical mixing of the solid catalysts of each of the previous generations, which catalysts were prepared according to claim 1.

4. The method according to claim 1, wherein the catalytic reaction is carried out with liquid, evaporated, or gaseous reactants.

5. The method according to claim 1, characterized in that the reactants for the catalytic reaction is supplied to several reactors and the product stream exiting the reactors is separately analyzed for each individual reactor.

6. The method according to claim 5, wherein for performing the catalytic reaction 5 to 1,000 reactors comprised of spaces with catalytically active material arranged therein are arranged parallel to one another or arranged in arrays, wherein the diameter of these spaces is 100 μm to 10 mm and the lengths are 1 mm to 100 mm.
7. The method according to claim 5 or 6, wherein, for a pre-set reactor length, the throughput of reactants is selected such that the desired degree of conversion is reached.
8. The method according to claim 6, wherein a monolithic block with several parallel channels, which can be closed selectively at the inlet or outlet side individually or in larger number also during the catalytic reaction, or a porous module having channels extending preferably parallel to the flow direction of the reaction mixture which channels can be selectively individually or in large number closed at the inlet or outlet side also during the catalytic reaction, is used as the reactor.
9. The method according to claim 1, wherein the reactants for the catalytic reaction are supplied to the reactors according to claims 6, 7, and 8, and wherein the composition of the product streams exiting the reactors is analyzed by a measuring sensor, wherein the measuring sensor is guided two-dimensionally across the exit cross-section of all reactors or the reactors are moved two-dimensionally relative to the measuring sensor and the portion of the product streams received by the measuring sensor is supplied to the analytical device.
10. The method according to claim 9, wherein the analytical device is a gas chromatograph, a mass spectrometer or another device used for the analysis of mixtures of gases and liquids.

11. The method according to claim 1 and claims 4 to 10, wherein suitable indicators are added to the reaction mixture, which indicate the presence of one or more educts or products, thus making possible the analysis within the mixture of reactants.

5

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Abstract

5 In the method for producing catalysts according to the
invention, in a first step (i) components are selected and
added to a library of substances. Mixtures of these individual
materials are then produced randomly by random selection. In
the second step (ii), the first generation of catalysts
10 produced is catalytically tested. Catalyst-optimised materials
from step (ii) are physically/chemically characterised for
reproducible production in step (iii) and form the basis for a
second generation of catalysts. This second generation is
produced gradually from the successful materials of the first
15 generation using biological evolutionary methods and subjected
to steps (ii) and (iii). For the second and subsequent
iterations, the most successful catalysts of all the
generations are taken as a basis in each case, the total
number of said catalysts being 1 to 50% of the catalysts of a
20 generation. The iterations are continued until no further
improvement is observed in the catalytic properties of the
materials in terms of activity/selectivity, for the reaction
concerned.

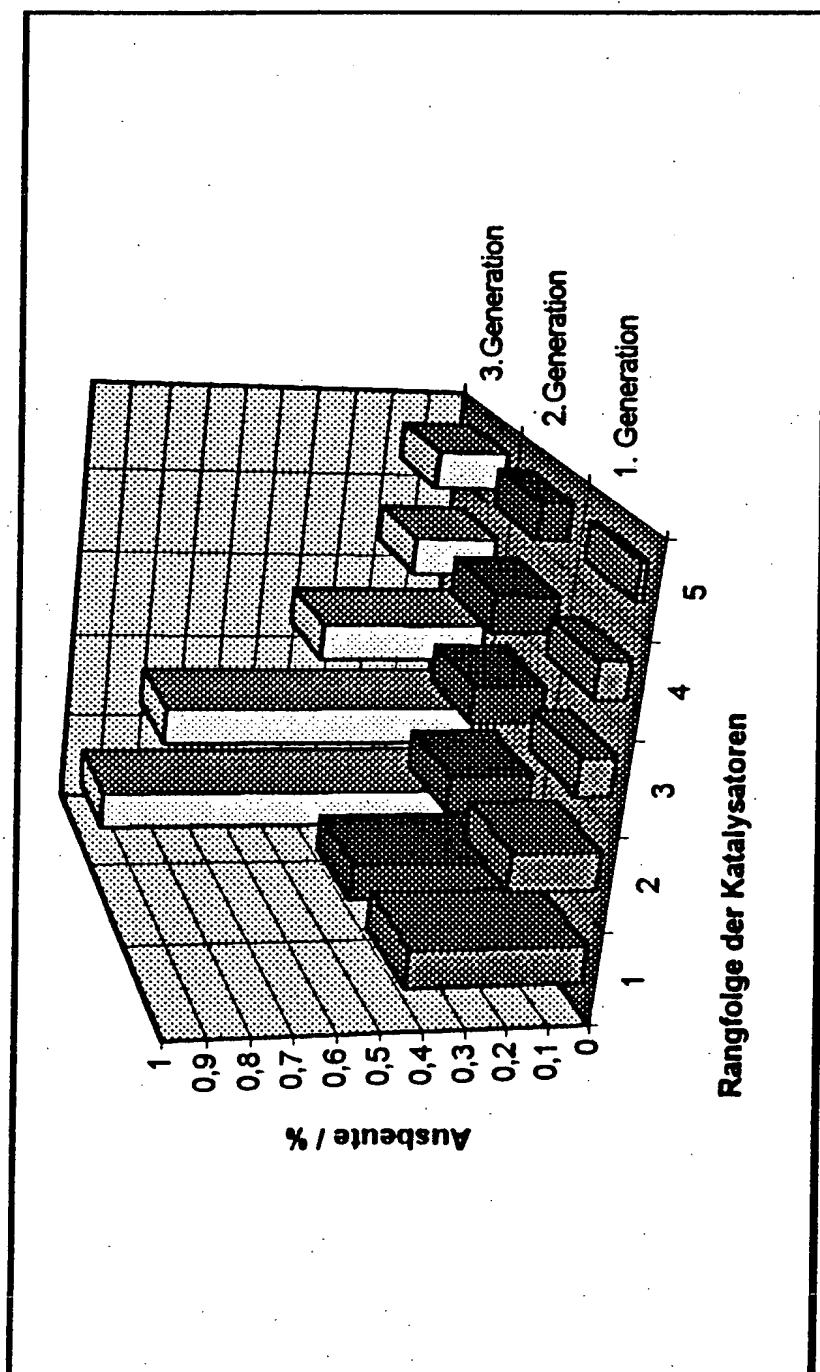


Fig. 1

I, Wolf-Jürgen Walter,

of, Schirnerstrasse 37, D-12524 Berlin, Germany

do hereby certify that I am well acquainted with the English and German languages and that the attached is a true translation into the English language of

Priority document DE 198 43 242.9

Signature

A handwritten signature in black ink, appearing to read 'Wolf-Jürgen Walter', written in a cursive style.

Dated this 14th day of November 2005